

## MOLECULAR CONFORMATION AND HYPERCONJUGATION. P-C-HYPERCONJUGATION AND THE CONFORMATION OF VINYL-, ALLYL-, PHENYL- AND BENZYLPHOSPHINES<sup>a,b,c</sup>

H. SCHMIDT and A. SCHWEIG\*

Fachbereich Physikalische Chemie der Universität, D-3350 Marburg/Lahn, Biegenstrasse 12, Germany

and

F. MATHEY and G. MÜLLER

Institut National de Recherche Chimique Appliquée, F-91-Vert-le-Petit, France

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**Abstract**—The photoelectron (PE) spectra of di-n-butylmethylphosphine, tri-n-butylphosphine, di-n-butylvinylphosphine, allyldi-n-butylphosphine, di-n-butylphenylphosphine, and benzyldi-n-butylphosphine, have been interpreted to exclude  $n/\pi$ -,  $d/\pi$ - and inductive interactions between the  $\alpha$ - and  $\beta$ -phosphinyl substituents and the  $\pi$ -electron systems. Instead, PC/ $\pi$  (hyperconjugative)-interaction has been detected in all these  $\pi$ -systems for the first time; the vinyl-, phenyl-, allyl- and benzylphosphines must exist in ground-state conformations which allow hyperconjugation. A comparison with corresponding vinyl- and allylsilanes suggests that, contrary to the vinyl-phosphines,  $d/\pi$ -conjugation is important in vinylsilanes. The CNDO/2-method is used to specify phosphine conformations more fully and to support the new conformational conclusions theoretically.

In early 1972, Weidner and Schweig<sup>1</sup> deduced the following from their analysis of photoelectron (PE) spectrum of allyltrimethylsilane: (i) The interaction between the  $\beta$ -silyl-group and the  $\pi$ -system in allyltrimethylsilane is hyperconjugative (SiC-hyperconjugation<sup>2,3</sup>) and not as others<sup>4</sup> believed  $d/\pi$ -or/and inductive. This Si-C/ $\pi$ -ground state-interaction can be measured directly from the location of the  $\pi$ -ionization band in the PE-spectrum of allyltrimethylsilane relative to the  $\pi$ -ionization band in the PE-spectrum of ethylene. (ii) The ground state conformation of allylsilanes is determined by the hyperconjugative interaction between the  $\beta$ -silyl group and the adjacent  $\pi$ -system meaning that such compounds exist in a gauche and not in a cis form. The energy difference between both forms was calculated to be 3.3 kcal/mole for allyltrimethylsilane using the CNDO/2 method<sup>5</sup> and a spd-basis. Hase and Schweig<sup>6</sup> suggested that the conformations of molecules and, in particular, of uncharged and non-radical molecules may be determined by hyperconjugation. (iii) Based on these results, PE-spectroscopy was proposed as a new method for establishing molecular conformations. Subsequently, Weidner and Schweig<sup>7</sup> applied their method of investigation to propene, vinylsilane, 3,3-dimethyl-1-butene, trimethyl-vinylsilane and 4,4-dimethyl-1-pentene pointing to the important rôle played by the d-AO's on silicon and simultaneously by CH-, SiH, CC- and SiC-hyperconjugation in determining the preferred conformation of these molecules. Thereafter Schweig *et al*<sup>8</sup> studied the GeC- and SnC-hyperconjugation<sup>9</sup> and the conformations of allylgermanes and -stannanes suggesting different hyperconjugative

ability of the CM (M = Si, C, Ge and Sn) bonding MO's with the ethylene  $\pi$ -MO. These aspects were later worked out more fully by Schweig *et al.*<sup>10</sup> and by Pitt.<sup>11</sup> The same procedure was successfully applied to allylmercuric chloride,<sup>12</sup> allyl and benzyl halides,<sup>13,14</sup> allylsulphides,<sup>15,16</sup> and to benzylsilanes, -germanes and -stannanes.<sup>10</sup> These investigations led to the first semi-quantitative proofs of hyperconjugation.<sup>10,12-14</sup>

Prior to our work on the interrelation between hyperconjugation and conformations adopted by neutral molecules, Taylor *et al.*<sup>17</sup> and Pitt<sup>18</sup> demonstrated from studies of charge transfer bands with TCNE of sterically rigid molecules that the  $\beta$ -silyl substituent effect is sensitive to the relative orientation of the SiC-bond and the nodal plane of the  $\pi$ -electron system. Simultaneously with our work a paper by Bach and Scherr<sup>19</sup> appeared suggesting that allylmercuric bromide exists in the minimal energy conformation that maximizes hyperconjugation and they later<sup>20</sup> used the same extended Hückel method to confirm the conclusions of Schweig *et al.*<sup>1,7,8</sup> regarding the conformations of Group IV allyl compounds. Following the work of Weidner and Schweig<sup>1</sup> on allyltrimethylsilane Bock *et al.*<sup>21</sup> abandoned their previous inductive explanation of the  $\beta$ -silyl effect and interpreted the PE-spectrum of allylsilane in terms of SiC-hyperconjugation and  $d/\pi$ -bonding, but wrongly assumed free rotation of the  $\beta$ -silyl substituent for allylsilane. Recently, all essential deductions made by Schweig *et al.*<sup>1,7</sup> on the rôle of  $\beta$ -silyl substituents in determining the ionization potentials and the conformation of allylsilanes were confirmed by the ab initio results of Horn and Murrell.<sup>22</sup> According to their results on allylsilane including d-AO's on silicon, the difference between parallel (cis) and perpendicular (i.e. nearly gauche) configurations of the  $\beta$ -silyl substituent amounts to 3.1 kcal/mole in excellent agreement with the CNDO/2 value obtained by Weidner and Schweig.<sup>1</sup>

Based on the aforementioned work,<sup>1,7,8,10,12-16</sup> it is now well established that the ground state conformation of

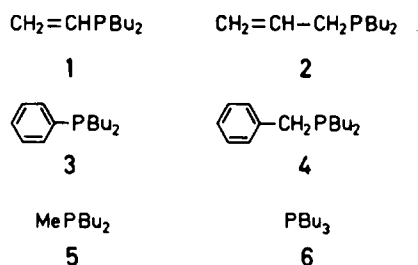
\*Theory and Application of Photoelectron Spectroscopy, Part 55. -Part 54: G. Lauer, C. Müller, K. W. Schulte, A. Schweig, G. Maier and A. Alzérreca, *Angew. Chem.*, in press.

<sup>b</sup>The work reported here was presented during the V International Conference of Organic Phosphorus Chemistry, Gdansk, 16-21 September 1974.

<sup>c</sup>Dedicated to Professor K. Dimroth on his 65th birthday.

vinyl, allyl, phenyl and benzyl compounds is widely determined by hyperconjugative interactions between the  $\pi$ -electron system and the substituents (especially substituents containing atoms of higher atomic number). Thus hyperconjugation constitutes a new force in addition to those discussed in a recent review by Wilson<sup>23</sup> on conformational studies on small molecules, namely (1) the double bond character due to resonance, (2) hydrogen bonding, (3) barrier forces, (4) steric repulsion, (5) electrostatic forces such as dipole-dipole, (6) valence bond stretching and bending forces, (7) inductive forces and (8) dispersion forces, which must necessarily be taken into account when discussing molecular conformations.

In this paper we use both the PE-procedure of Schweig *et al.*<sup>1,7,8,10,12-16</sup> and quantum chemical calculations of the valence-electron-type, namely CNDO/2<sup>5</sup> and CNDO/S,<sup>24</sup> to study the conformations of di-n-butylvinylphosphine 1 allyl di-n-butylphosphine 2, di-n-butylphenylphosphine 3 and benzyl di-n-butylphosphine 4. Hitherto, no other



attempts to establish the conformations of vinyl-, allyl-, phenyl- and benzylphosphines have been reported. Likewise, apart from a recent ESR study by Mistra and Symons,<sup>25</sup> the field of PC-hyperconjugation seems to be unexplored. In particular, the question whether PC-hyperconjugative effects will also be important for molecules remains to be settled. Later in this paper we show that, indeed, the conformations of compounds 1, 2 and 4 are determined by hyperconjugation. Furthermore, the ability of the PC-bonding MO to undergo conjugative interactions with  $\pi$ -MO's (as measured by the corresponding interaction integral) is quantitatively established using a semiquantitative LCMO-approach and compared with the corresponding abilities of other bonding MO's previously explored by Schweig *et al.*<sup>1,7,8,10,12-16</sup>

#### INTERPRETATION OF THE PHOTOELECTRON SPECTRA

Figures 1-3 show the PE-spectra of di-n-butyl methylphosphine 5, tri-n-butylphosphine 6, di-n-butyl vinylphosphine 1, allyl di-n-butylphosphine 2, di-n-butyl phenylphosphine 3, and benzyl di-n-butylphosphine 4. The two saturated phosphines 5 and 6 serve as model compounds for the determination of the energy of the phosphorus lone pair (n)-MO and of the PC-bonding MO's. From previous experience with the interpretation of the PE-spectra of other saturated phosphines, namely trimethylphosphine 7<sup>26,27</sup> and n-butylphospholane 8<sup>28</sup> (the corresponding ionization potentials and assignments are given below), and in accordance with the measured

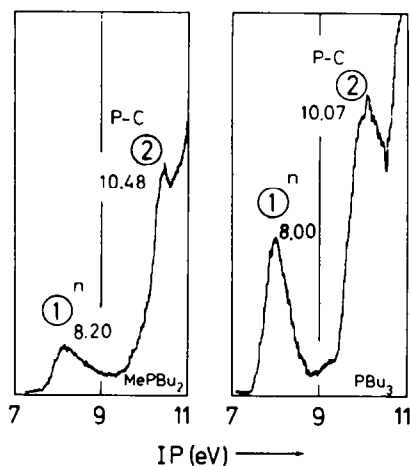
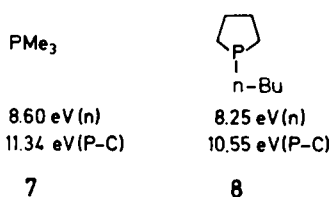


Fig. 1. Photoelectron spectra of di-n-butyl methylphosphine 5 and tri-n-butylphosphine 6 with interpretation. The numbers associated with each band are vertical ionization potentials.

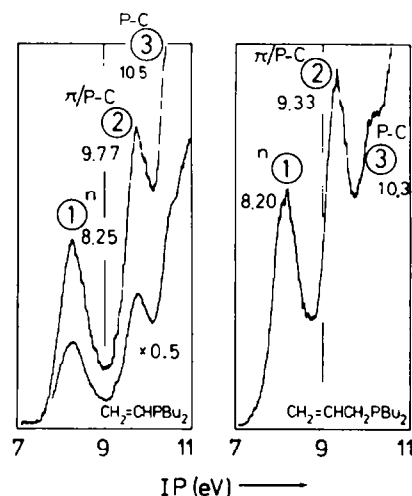


Fig. 2. Photoelectron spectra of di-n-butyl vinylphosphine 1 and allyl di-n-butylphosphine 2 with interpretation. The numbers associated with each band are vertical ionization potentials.

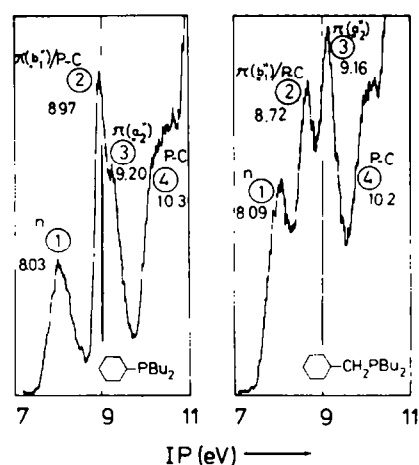


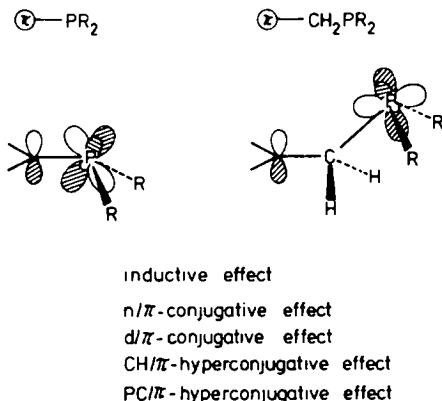
Fig. 3. Photoelectron spectra of di-n-butyl phenylphosphine 3 and benzyl di-n-butylphosphine 4. The numbers associated with each band are vertical ionization potentials.

relative intensities band 1 in the spectra of **5** and **6** must be assigned to ionization from the lone pair ( $n$ )-MO and 2 to ionization from the two PC-MO's which appear to be nearly degenerate for **5** and **6** just as for **7** and **8**. The PE-bands in the spectra of the corresponding vinyl- and allyl compounds **1** and **2** can be clearly assigned by comparison with the spectra of the saturated phosphines **5** and **6**. Accordingly, bands 1 and 3 in the spectra of **1** and **2** are due to ionizations from the  $n$  and a PC-MO respectively, while the remaining band 2 in both spectra must be ascribed to an antibonding combination between the ethylene  $\pi$ - and a mainly PC-localized  $\sigma$ -MO.

Due to this interaction (for a detailed discussion, see the next section) the PC/ $\pi$ -ionization is considerably shifted to lower potentials relative to both the PC-ionization in the saturated phosphines **5** and **6** and the ethylene  $\pi$ -ionization occurring at 10.51 eV.<sup>29</sup> Band assignments in the spectra of the phenyl and benzyl compounds **3** and **4** can be made in an analogous manner. Bands 1 and 4 must be ascribed to the  $n$  and PC-ionizations, respectively and bands 2 and 3 arise from the two highest occupied benzene  $\pi$ -MO's. Here again, one of these  $\pi$ -ionizations, the  $\pi$ ("b<sub>1</sub>")-ionization, occurs at appreciably lower ionization potentials than in benzene (9.25 eV<sup>29</sup>) due to hyperconjugative PC/ $\pi$ -interaction (for a detailed discussion, see the next section).

#### DEDUCTIONS FROM THE SPECTRAL DATA

Before attempting an interpretation of the present results a brief review of the types of interactions (illustrated below) available to systems such as **1-4** is



given. First, there is a possible mutual inductive polarization of the interacting groups ( $\pi$  and  $\text{PR}_2$  or

$\text{CH}_2\text{PR}_2$ ). Since the inductive effects of vinyl and phenyl groups are known to be low, we have to consider only the possible inductive effects exerted by the phosphinyl groups. Second, there may be conjugative interaction between the  $\pi$ -electron system and the  $n$ -MO and the  $d$ -AO's on phosphorus (i.e.  $n/\pi$ -conjugation or  $d/\pi$ -conjugation, respectively) and hyperconjugative interaction between the  $\pi$ -electron system and  $\text{CH}$ - and  $\text{PC}$ -MO's (i.e.  $\text{CH}/\pi$ - and  $\text{PC}/\pi$ -conjugation). The PE-results of the present paper in conjunction with suitable quantum chemical calculations permit us to differentiate between the different interaction mechanisms and to trace back the observed PE-shifts discussed in the preceding section to  $\text{CH}/\pi$ - and  $\text{PC}/\pi$ -conjugation.

The correlation diagrams of Figs. 4 and 5 show the measured orbital energies of the vinyl and allyl compounds **1** and **2** on the one hand, and of the phenyl and benzyl compounds **3** and **4** on the other, correlated with the corresponding  $\pi$ -, PC- and  $n$ -MO's in suitably chosen model compounds, namely ethylene or benzene and di- $n$ -butylmethylphosphine **5**.<sup>4</sup> The diagrams reveal at once that there is only a small (if any)  $n/\pi$  interaction in both series of compounds (**1** and **2** and **3** and **4**, respectively). This result is in full accordance with preceding work on dimethylphenylphosphine **9** by Schäfer and Schweig<sup>30</sup> and on 1-phenylphosphole **10** and 2,5-dimethyl-1-phenylphosphole **11** as well as on a series of 1-alkylphospholes **12-15** by Schweig *et al.*<sup>28,31</sup> Figure 5 further shows that the  $\pi$ ("a<sub>2</sub>") MO (for a representation of the  $\pi$ ("a<sub>2</sub>") and  $\pi$ ("b<sub>1</sub>") MO's, see below) lies at nearly the same energy in **3** as in benzene. This is in harmony with preceding work by Schweig *et al.*<sup>1,7,8,10,12-16</sup> and thus a reliable indication that the inductive effects of the  $\text{CH}_2\text{PR}_2$  and  $\text{PR}_2$  substituents are negligible.

<sup>4</sup>We calculated the relaxation energies of the  $n$ -ionic states using an unrestricted open-shell CNDO/S method. We obtained for trimethylphosphine **7** = 0.22 eV, for dimethyl vinylphosphine **22** = 0.30 eV, for allyl dimethylphosphine **17** = 0.22 eV, for dimethyl phenylphosphine **24** = 0.26 eV, and for benzyl phosphine **20** = 0.27 eV. For both the  $n$ - and  $\pi$ -ionic states the total Koopmans' defects (i.e. the ionic relaxation energies plus the difference in correlation energies between the ionic and the molecular ground states) have also been estimated (G. Lauer and A. Schweig, to be published). These total defects are virtually as equal in the series of the studied phosphines mentioned above as are the presented relaxation energies alone. In addition, the amounts of the total defects are somewhat smaller. All these results suggest that the conclusions drawn throughout this paper are actually unaffected by possible deviations from Koopmans' theorem.

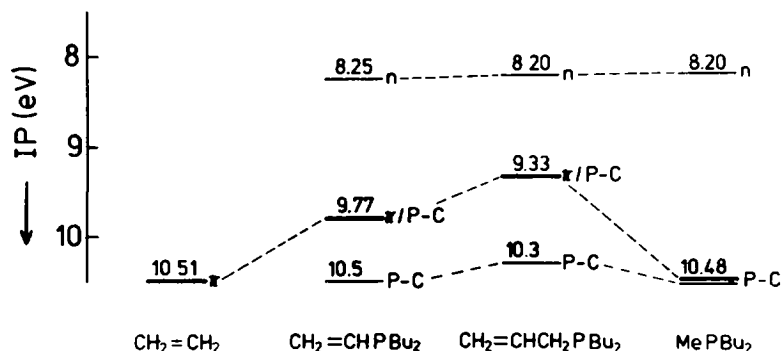


Fig. 4. Measured correlation diagram for the highest occupied MO's of ethylene, di- $n$ -butylvinylphosphine **1**, allyl di- $n$ -butylphosphine **2**, and di- $n$ -butyl methylphosphine **6**. The numbers shown above the levels are vertical ionization potentials.

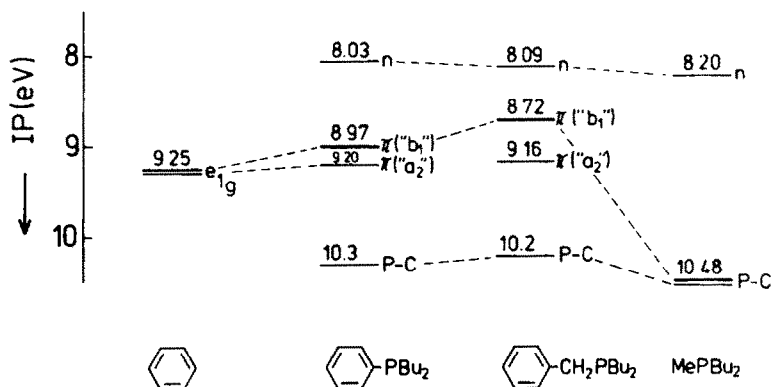
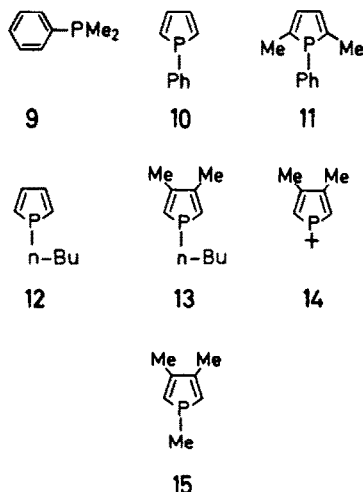
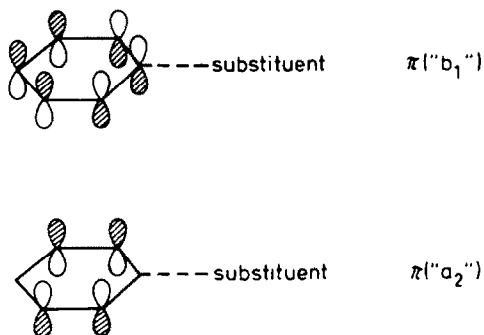


Fig. 5. Measured correlation diagram for the highest occupied MO's of benzene, di-n-butyl phenylphosphine 3, benzyl di-n-butylphosphine 4, and di-n-butyl methylphosphine 6. The numbers shown above the levels are vertical ionization potentials.

Now we turn to the two remaining mechanisms of interaction, i.e. the hyperconjugative and  $d/\pi$ -interaction mechanisms. The hyperconjugative interaction between



the occupied  $\pi$ - and CH- and PC-MO's leads to a destabilized antibonding linear combination (as seen in the PE spectra) and a bonding combination (hidden under



the  $\sigma$ -continuum and therefore not seen in the spectra). On the other hand, mixing of the unoccupied d-AO's on phosphorus with the occupied  $\pi$ -MO must stabilize the  $\pi$ -MO. Thus, if there is no hyperconjugation in 1 to 4 but just  $d/\pi$ -conjugation, the ethylene  $\pi$ -MO in 1 and 2 and the benzene  $\pi$ (" $b_1$ ")-MO in 3 and 4 would be stabilized relative to the ethylene- and benzene  $\pi$ -MO's, respectively. On the other hand, in the presence of only

hyperconjugative interaction strongly destabilized PC/ $\pi$ -mixed MO's in 1 and 3 and PC/ $\pi$ , and CH/ $\pi$ -mixed MO's in 2 and 4 should occur. As must be stressed, however, PC/ $\pi$ -mixing in 2 and 4 is only allowed by symmetry for the *gauche*-forms of these molecules (for illustrations of



the *gauche*- and *cis*-form in case of 2, see below). As we recognize from Figs. 4 and 5 the hyperconjugative interaction discussed above predominates in all molecules, 1-4. Obviously, this interaction is particularly efficient in 1 and 2 because of the near degeneracy of the two interacting  $\pi$ - and PC-MO's.

If  $d/\pi$ -interaction is important at all, we should expect that this type of interaction should show up at least in the spectral data of the vinyl and phenyl compounds 1 and 3 since only in these molecules can the d-AO's on the phosphorus atom directly interact with the adjacent  $\pi$ -MO's. We now present two arguments indicating that  $d/\pi$ -effects are insignificant with the phosphines studied in this paper. One argument may be derived from the n-MO energies shown in Figs. 4 and 5. Provided that  $d/\pi$ -bonding was significant, additional charge would accumulate on the phosphorus atom. As a consequence the n-MO in 1 and 3 would considerably increase in energy as compared with their counterparts in 2, 4, 5 and 6. Such an effect is not observed. A second argument becomes obvious from the results of CNDO/S<sup>2</sup>-calculations with and without inclusion of d-AO's on phosphorus depicted in Figs. 6 and 7. Accordingly, d-AO's play no significant rôle for the orbital energies (i.e. the Koopmans<sup>32</sup> ionization potentials) of the phosphines studied.

After showing that the observed changes in the PC/ $\pi$ -orbital energies in 1 and 2 and of the  $\pi$ (" $b_1$ ")-orbital energies in 3 and 4 are due to PC/ $\pi$ -conjugation we may now start to put these interactions on a more quantitative basis. Starting from the model assumption<sup>33</sup> that the " $\pi$ -electron-structure" of 1-4 can be described well by the interaction of the localized  $\pi$ -MO (ethylene  $\pi$ -MO (-10.51 eV<sup>29</sup>) for 1 and 2 and  $\pi$ (" $b_1$ ")-MO for 3 and 4 (-9.25 eV<sup>29</sup>) and "pseudo"- $\pi$ -MO's localized on the PBu<sub>2</sub> and CH<sub>2</sub>PBu<sub>2</sub> group (-10.48 eV), and further assuming that in 2 and 4 the CH/ $\pi$ - and PC/ $\pi$ -interactions can be treated independent on each other we may use the

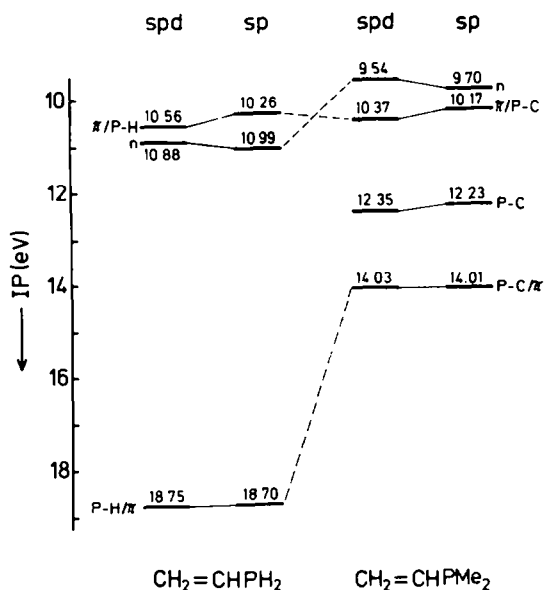


Fig. 6. Orbital energies calculated with and without inclusion of 3d-AO's on phosphorus by the CNDO/S method for the most stable conformations (see text) of vinylphosphine 21 and dimethyl vinylphosphine 22.

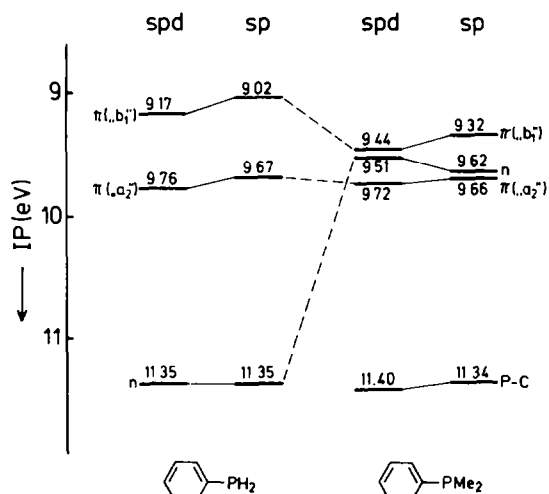
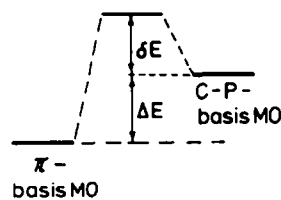


Fig. 7. Orbital energies calculated with and without inclusion of 3d-AO's on phosphorus by the CNDO/S method for the most stable conformations (see text) of phenylphosphine 23 and dimethyl phenylphosphine 24.

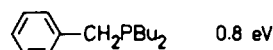
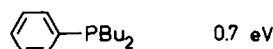
variation method to derive the CP/ $\pi$ -interaction integrals  $H_{\pi\pi}$ . This is achieved by first correcting the measured orbital destabilizations  $\delta E$  by 0.31 eV for 2 and 0.12 eV for 4 to eliminate the CH/ $\pi$ -effect as previously done by Schmidt and Schweig,<sup>13,14</sup> and then by introducing the measured  $\delta E$ -values for 1 and 3 and the corrected  $\delta E$ -values for 2 and 4 together with the corresponding basis orbital-energy differences  $\Delta E$  in the equation shown below (along with a scheme illustrating the hyperconjugative interaction) we obtain the  $H_{\pi\pi}$ -values summarized below the equation. These values are nearly equal for all four molecules investigated. Finally, we should like to comment on this interesting finding. First, we see that the PC/ $\pi$ -interaction integrals are somewhat smaller than the corresponding M(C, Si, Ge, Sn)C/ $\pi$ -interaction integrals (1.1–1.2 eV) recently determined by Schweig *et al.*<sup>10</sup> We further see that, in full agreement with the preceding results



$$H_{\pi\pi} = [\delta E (\delta E + \Delta E)]^{1/2}$$

$$\text{CH}_2 = \text{CHPBu}_2 \quad 0.8 \text{ eV}$$

$$\text{CH}_2 = \text{CHCH}_2\text{PBu}_2 \quad 0.9 \text{ eV}$$



by Schmidt and Schweig<sup>13,14</sup> and by Schweig *et al.*,<sup>10</sup> the PC/ $\pi$ -integrals are the same for the pairs vinyl/phenyl and allyl/benzyl. However, the most exciting result is: the interaction integrals are almost the same in the vinyl/phenyl case as in the allyl/benzyl case. This result sharply differs from an analogous silicon example, where the SiC/ $\pi$ -

$$\text{CH}_2 = \text{CH}_2 \quad \text{SiMe}_2$$

$$10.51 \text{ eV} \quad 10.57 \text{ eV}$$

$$\text{H}_2\text{C} = \text{CHSiMe}_3 \quad \text{CH}_2 = \text{CHCH}_2\text{SiMe}_3$$

$$9.8 \text{ eV} \quad 9.0 \text{ eV}$$

$$H_{\pi\pi} = [\delta E (\delta E + \Delta E)]^{1/2}$$

$$\text{CH}_2 = \text{CHSiMe}_3 \quad 0.74 \text{ eV}$$

$$\text{CH}_2 = \text{CHCH}_2\text{SiMe}_3 \quad 1.23 \text{ eV}$$

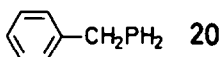
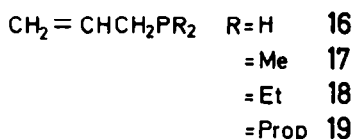
interaction integral in trimethylvinylsilane is considerably lower than the corresponding quantity in the allyltrimethylsilane (the relevant ionization potentials and the derived interaction integrals  $H_{\pi\pi}$  are summarized below). There are two ways to account for the lower vinyl value either by arguing that the two basis MO's (SiC and  $\pi$ ) are more distant in the vinylsilane than in the allylsilane because of the longer SiC-bond (1.86 Å<sup>34</sup>) as compared to the CC-bond (1.54 Å<sup>34</sup>) or by referring to appreciable d/ $\pi$ -bonding as Weidner and Schweig<sup>7</sup> did. We feel that the present example of di-n-butyl vinyl-phosphine points to the latter direction; any significant 3d-contribution on phosphorus in the phosphines seems to be unlikely (as was discussed above) and simultaneously the PC-bond length (1.84 Å<sup>34</sup>) is nearly the same as the SiC-length. The bond length-effect as an explanation for the different influence exerted by  $\alpha$ -silyl- and  $\beta$ -silyl groups and had been favoured by Pitt.<sup>18</sup> In his more recent paper,<sup>11</sup> however, he turned to the combined SiC/ $\pi$ - and d/ $\pi$ -mechanisms as proposed by Weidner and Schweig.<sup>7</sup>

The results obtained so far clearly prove that both the allyl- and benzylphosphines 2 and 4 and the vinyl- and

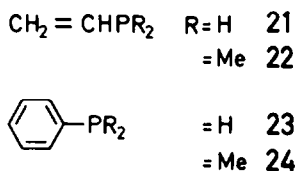
phenylphosphines **1** and **3** must exist in conformations which allow efficient CP/ $\pi$ -conjugation. It is the purpose of the following CNDO/2 calculations to specify more closely these conformations and to further confirm theoretically whether indeed hyperconjugation determines these conformations.

#### DEDUCTIONS FROM CNDO/2-CALCULATIONS

Figures 8 and 9 display the conformational diagrams for some allylphosphines, namely allylphosphine (**16**: R = H), allyldimethylphosphine (**17**: R = Me) and allyldiethylphosphine (**18**: R = Et) and benzylphosphine **20**. Figures



**10** and **11** show the corresponding diagrams for vinylphosphine (**21**: R = H) and dimethyl vinylphosphine (**22**: R = Me) and phenylphosphine (**23**: R = H) and dimethyl phenylphosphine (**24**: R = Me), respectively. In all cases



the total energy is plotted against the angle  $\alpha$  specified in the formula shown in each Figure (curves drawn as  $\circ$ ,  $\bullet$ ,  $\times$ ,  $\text{---}$ ). In case of allylphosphine **16** the gauche-form ( $\alpha = 100^\circ$ ) is only 0.24 kcal/mole more stable than the cis-form ( $\alpha = 0^\circ$ ). For the more substituted allylphosphines **17** and **18** the gauche-form is now by far the most stable one. The same is valid for the propyl-substituted allylphosphine **19** not shown in Fig. 8. Benzylphosphine (see Fig. 9) is also predicted to prefer strongly a gauche-conformation ( $\alpha = 80^\circ$ ) the cis-form ( $\alpha = 0^\circ$ ) being less stable by 1.77 kcal/mole. Both vinylphosphines **21** and **22** exist only in the one conformation with the two PR-bonds directed away from the  $\pi$ -electron system with its nodal plane bisecting the PRP-angle (see Fig. 10). The situation is quite analogous to the dimethylphenylphosphine **24** as Fig. 11 indicates.\* The unsubstituted phenylphosphine **23**, however, prefers quite a different conformation with  $\alpha = 137.5^\circ$ .

There is a very elegant way to investigate whether the predicted stable conformations in Figs. 8–11 are indeed determined by hyperconjugation. The method has first been described by Baird<sup>35</sup> and has recently been used in a study of conformational problems by Hase and Schweig.<sup>6</sup> The method was meanwhile extended by Schweig *et al.*<sup>6,36–40</sup> to the investigation of the mutual conjugative,

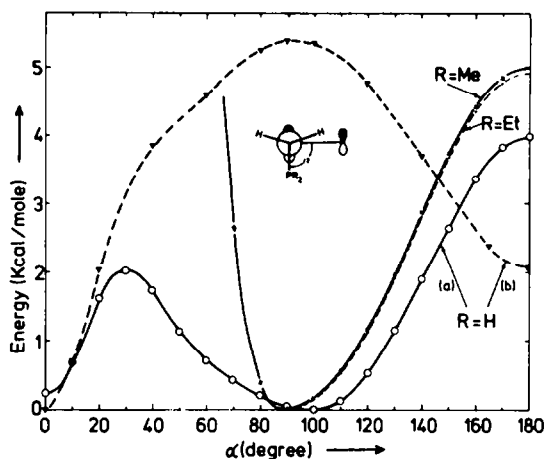


Fig. 8. Plots of the total energy with ( $\text{---}\Delta\text{---}$ ) and without ( $\text{---}\circ\text{---}$ ,  $\text{---}\times\text{---}$ , and  $\text{---}\text{---}$ ) conjugative interruption between the vinyl and the  $\beta$ -phosphinyl ( $\text{CH}_2\text{PR}_2$ )-groups vs. the angle  $\alpha$  for R = H **16**. For R = Me **17** and R = Et **18** the total energy without conjugative decoupling is plotted only. The calculations are performed using the CNDO/2-method.

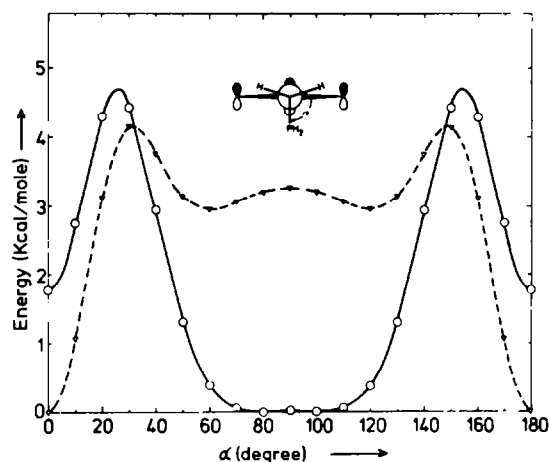


Fig. 9. Plots of the total energy with ( $\text{---}\Delta\text{---}$ ) and without ( $\text{---}\circ\text{---}$ ) conjugative interruption between the phenyl and the  $\beta$ -phosphinyl ( $\text{CH}_2\text{PH}_2$ )-groups vs. the angle  $\alpha$  for benzylphosphine **20**. The calculations are performed by use of the CNDO/2 method.

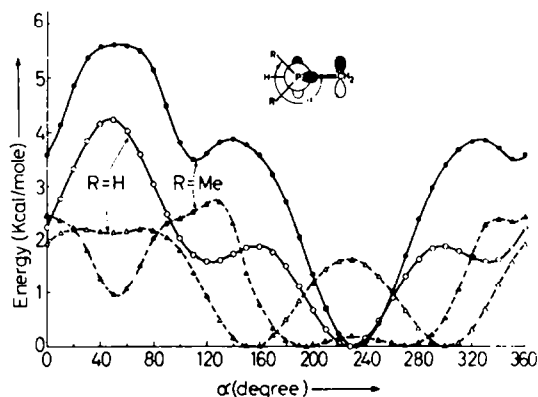


Fig. 10. Plots of the total energy with ( $\text{---}\Delta\text{---}$ ,  $\text{---}\blacktriangle\text{---}$ ) and without ( $\text{---}\circ\text{---}$ ,  $\text{---}\bullet\text{---}$ ) conjugative interruption between the vinyl and the  $\alpha$ -phosphinyl ( $\text{PR}_2$ ) groups vs. the angle  $\alpha$  for R = H **21** and R = Me **22**. All values were obtained by the CNDO/2 method.

\*Recent Kerr-effect measurements on dimethyl (4-methylphenyl) phosphine confirm that the most stable conformation of this molecule is the one predicted for dimethyl phenylphosphine **24** in this work; reported by A. N. Vereshchagin (A. E. Arbutov, Institute of Organic and Physical Chemistry, Kazan Branch of the USSR Academy of Science, Kazan, USSR) during the V International Conference of Organic Phosphorus Chemistry, Gdansk, 16–21 September 1974.

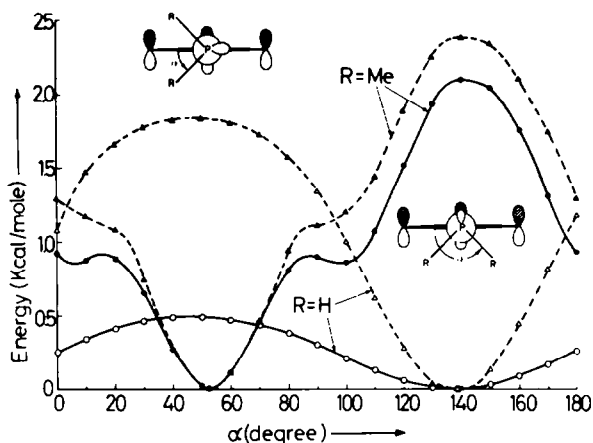
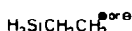


Fig. 11. Plots of the total energy with (--- $\Delta$ ---, --- $\blacktriangle$ ---) and without (— $\circ$ —, — $\bullet$ —) conjugative interruption between the phenyl and the  $\alpha$ -phosphinyl ( $\text{PR}_2$ ) groups vs. the angle  $\alpha$  for  $\text{R} = \text{H}$  23 and  $\text{R} = \text{Me}$  24. The calculations were carried out by using the CNDO/2 method.

steric and inductive effects existing between two coupled localized systems and successfully applied to  $\beta$ -silyl and  $\beta$ -germyl ions<sup>5</sup> 25 and 26, tropone<sup>36</sup> 27, bicyclo[4.2.1]nona-2,4,7-trien-9-one 28,<sup>37</sup> 3,3,6,6-tetramethyl-1-thiacycloheptyne 29,<sup>38</sup> cyclopropanones<sup>39</sup> 30 and 31 and thiirene dioxide<sup>40</sup> 32. The essence of the procedure is that conjugative interactions between MO's localized on two different parts of a molecule can be cut off so that only the inductive and steric interactions remain. Just this was done for the system studied in Figs.

mined by hyperconjugation but presumably by steric interactions (between the H-atoms of the  $\text{PR}_2$  grouping and the ortho H-atoms of the ring). As a matter of fact, the variation of the calculated hyperconjugation energy (i.e. the difference in total energy with hyperconjugation and without hyperconjugation) with the rotational angle  $\alpha$  is, for 23 and 24, 10 times smaller than for the allylphosphines 16 to 19, 7 times smaller than for the benzylphosphine 20, and 5 times smaller than for the vinylphosphines 21 and 22.



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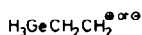
27



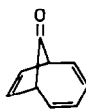
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## CONCLUSIONS

In summary, the results of this report have established the following important points: (i) Photoelectron spectroscopy is a very powerful method for establishing the molecular conformations of simple molecules. The procedure proposed in 1972 by Schweig *et al.* proved, in the present work, very successful in finding the molecular conformations of vinyl, allyl, phenyl and benzylphosphines. The method constitutes a new contribution to the field of molecular conformational analysis. (ii) In preceding papers Schweig *et al.* first pointed to the strong consequences of hyperconjugation for molecular conformations (in particular, uncharged and nonradical systems). In the present paper they demonstrate that the conformations of vinyl-, allyl- and benzylphosphines are determined by CP-hyperconjugation. (iii) CP-hyperconjugation hitherto wholly neglected in discussing properties of organic phosphorus compounds must be taken into account as the present report shows. This result is of fundamental importance for organic phosphorus chemistry.

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## APPENDIX

As far as we know the phosphines 2 and 5 were previously unknown; the data are given. Me PBu, 5: B.p. 66–68°C/11 mm Hg, Synthesis from  $\text{MePCl}_2 + 2\text{BuMgBr}$  (ether) in very low yield, NMR (external TMS)  $\text{CH}_3$ ,  $\delta = 0.77$  ppm (no  $\text{CH}_3$ -P coupling),  $\text{CH}_2$   $\delta = 1.19$  ppm.  $\text{CH}_2 = \text{CH}-\text{CH}_2\text{PBu}$ , 2: B.p. 93°C/8 mm Hg. Synthesis from  $\text{Bu}_2\text{POEt} + \text{CH}_2 = \text{CH}-\text{CH}_2\text{MgCl}$  (ether, 10 h) yield 40%. NMR (external TMS)  $\text{CH}_3$ ,  $\delta = 0.77$  ppm,  $\text{CH}_2(\text{nBu})$   $\delta = 1.20$  ppm,  $\text{CH}_2\text{P}$   $\delta = 2.03$  ppm, J (H-P) = 7.3 Hz, =CH  $\delta = 5.62$  ppm, = $\text{CH}_2$   $\delta = 4.88$  and 4.65 ppm (non-equivalent).

8–11 by interrupting the conjugation between the AO's of the  $\pi$ -electrons systems and all remaining AO's contributed by the atoms of the  $\text{PR}_2$ - or  $\text{CH}_2\text{PR}_2$ -groups. In this manner we cut off all conjugative  $\text{PR}_2/\pi$  and  $\text{CH}_2\text{PR}_2/\pi$  interactions simultaneously. Since we showed above (see the preceding section) that the  $d/\pi$ - and  $n/\pi$ -interactions are insignificant we obtain now the total energy without hyperconjugation as a function of the angle  $\alpha$ . The thus evaluated curves (--- $\Delta$ ---; --- $\blacktriangle$ ---) are additionally presented in Figs. 8–11. The latter curves have maxima at the regions where the most stable rotamers exist (i.e. the regions where the total energy with inclusion of hyperconjugation shows minima) with the exception of the phenylphosphines 23 and 24 which means that the conformations of the latter compounds are not deter-

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